WSC - CAM – V D

Quality Assurance and Quality Control Requirements and Performance Standards for **SW-846 Method 8021B, Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors**, for the Massachusetts Contingency Plan (MCP)

Document Status: Final

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Document Chronology

Revision	Status	Date
0	Public Comment Draft	31 January 2002
1	Final	30 May 2003
2	Final	28 May 2004

V. Gas Chromatographic Methods

D. Quality Assurance/Quality Control (QA/QC) Requirements and Performance Standards for SW-846 Method 8021B

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1.0 QA/QC Requirements for SW-846 Method 8021B

1.1 Method Overview

Method 8021B is a high resolution gas chromatographic (GC) method that provides for the analysis of volatile organic compounds in water, soil, sediment and waste samples. Standard Photoionization (PID) and Hall Electrolytic Conductivity (HECD) detectors are used in series to identify and quantify the target analytes.

It is strongly recommended that the use of Method 8021B be limited to the quantification of a limited list of pre-selected (and known) volatile contaminants of concern at disposal sites that have been previously characterized with qualitative certainty (i.e., SW-846 Method 8260B) and/or have a known and un-complex site history. Even under these circumstances, if the laboratory encounters additional chromatographic peaks **with a peak height greater than 50% of the appropriate detector surrogate** (See Table V D-1, Surrogates) that are not associated with calibrated target analytes, then these findings must be reported by the laboratory to the LSP that requested the analysis in the Environmental Laboratory case narrative. Appropriate response actions to identify and quantify the reported unidentified peaks, to include re-analysis of the samples using SW-846 Method 8260B, must be considered by the data user.

When using a PID/HECD-GC system to analyze unfamiliar samples, compound identifications must be supported by two column confirmation or verified by at least one additional determinative technique such as SW-846 Method 8260B. The GC system may also be configured in a single detector mode if the analysis of only halogenated (HECD) or only aromatic (PID) compounds are requested by the data user.

1.1.1 Reporting Limits for SW-846 Method 8021B

The reporting limit (RL) for SW-846 Method 8021B for an individual compound is somewhat instrument dependent and is also dependent on the choice of sample preparation/introduction method and/or percent (%) solids of the sample. Using standard Photoionization and Hall Electrolytic Conductivity detectors and the purge-and-trap technique, reporting limits should be approximately 1 µg/kg (wet weight) for low-level soil/sediment samples (* Based on 1:1 ratio of methanol to soil and analysis of 100 uL of methanol extract in 5 ml of water), 0.1 **mg**/kg (wet weight) for wastes (sample usually requires special pre-treatment and/or dilution prior to analysis), and 1 µg/L for groundwater (based on a 5 mL purge volume). No matter which instrument is used, reporting limits for SW-846 Method 8021B will be proportionately higher for samples that require dilution, or when a reduced sample size is used to avoid saturation of the detector.

In most cases, the reporting limits for Method 8021B associated with methanol preservation of soils and sediments should be adequate to assure regulatory compliance and a low-level preservative option in lieu of methanol will not be required.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for VOCs analyzed in support of MCP decision-making

are presented in Appendix V D–1 of this document and Appendix VII-A, WSC-CAM -VIIA, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 General Quality Control Requirements of SW-846 Method 8021B

Each laboratory that uses SW-846 Method 8021B is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks to confirm acceptable continuing performance, and the analysis of laboratory control spikes (LCSs) and LCS duplicates to assess analytical accuracy and precision. Matrix spikes (MS), matrix spike duplicates (MSD) or Matrix duplicates may also be used to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user.

Laboratories must document and have on file an Initial Demonstration of Proficiency for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.5 and Table V D-1 of this method. Procedural requirements for performing the Initial Demonstration of Proficiency can be found in SW-846 method 8000B (Section 8.4) and SW-846 Method 8021B (Section 8.3). The data associated with the Initial Demonstration of Proficiency should be kept on file at the laboratory and made available to potential data-users on request. The data associated with the Initial Demonstration of Proficiency for SW-846 Method 8021B must include the following:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM–V D, Table V D-1
Continuing Calibration	WSC-CAM–V D, Table V D-1
Method Blanks	WSC-CAM–V D, Table V D-1
Average Recovery	SW-846 Method 8000, Section 8.4
% Relative Standard Deviation	SW-846 Method 8000, Section 8.4
Surrogate Recovery	WSC-CAM–V D, Table V D-1
Internal Standards	WSC-CAM–V D, Table V D-1

Note: Because of the extensive analyte list and number of QC elements associated with the Initial Demonstration of Proficiency, it should be expected that one or more analytes may not meet the performance standard for one or more QC elements. Under these circumstances, the analyst should attempt to locate and correct the problem and repeat the analysis for all non-conforming analytes. All non-conforming analytes along with the laboratory-specific acceptance criteria should be noted in the Initial Demonstration of Proficiency data provided.

It is essential that laboratory-specific performance criteria for LCS, LCS duplicate and surrogate recoveries also be calculated and documented as described in SW-846 Method 8000B, Section 8.7. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of

documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table V D-1 to assess analytical trends (i.e., systematic bias, etc) and improve overall method performance by preempting potential non-conformances.

For SW-846 Method 8021B, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed in Table V D-1. It should be noted that the performance standards listed in Table V D-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. In some cases, the standard laboratory acceptance criteria for the various QC elements may have to be modified to accommodate more rigorous project-specific data quality objectives prescribed by the data user. The laboratory may be required to modify routine sample introduction and/or analytical conditions to accommodate project-specific data quality objectives.

This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs (GCs) and skilled in the interpretation of gas chromatograms for individual target analytes and multi-component mixtures of volatile organics in environmental matracies. Each analyst must demonstrate the ability to produce acceptable quantitative and qualitative results for individual target analytes and multi-component mixtures of purgeable volatile organics at low µg/L or µg/kg concentrations with this method.

1.2 Summary of Method

Method 8021B provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. The volatile compounds are introduced directly on to a temperature-programmed, wide-bore capillary column by the purge-and-trap method or other methods described in Section 1.4 below. The separated analytes eluted from the column are then detected by a PID or HECD operating in series. Quantitation is accomplished by comparing the response of a each analyte to the response of a corresponding standard determined from a five-point calibration curve.

1.3 Method Interferences

1.3.1 Chemical Contaminants

Refer to SW-846 Methods 5000 and 8000 for general precautions to minimize interferences with volatile organic analyses. Major contaminant sources for SW-846 Method 8021B include,

but are not limited to, halogenated and aromatic volatile organic contaminants in the laboratory, purging gas and sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of

contaminants. When potential interfering peaks are noted in blanks, the analyst should determine their cause. Corrective actions may include changing the purge gas source and/or regenerating the molecular sieve purge gas filter. **Subtracting blank values from sample results is not permitted.** If the laboratory determines that reporting values without correcting for the blank may result in a false positive result for a sample, the laboratory should fully explain and justify this condition in the laboratory case narrative.

1.3.2 Cross-contamination

Cross-contamination may occur when any sample is analyzed immediately after a sample containing a significantly higher concentration of halogenated and/or aromatic volatile organic compounds. After the analysis of a sample containing significantly higher concentrations of these volatile organic compounds than other samples in the analytical batch, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established, a priori. In addition, samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, may also present potential for cross-contamination.

1.3.3 Analytical Carryover

Many analytes exhibit low purging efficiencies when sample volumes greater than 5-mL are used. This may result in significant amounts of these analytes remaining in the sample purge vessel after analysis. Refer to Section 3.0 of SW-846 Method 8021B for a description of approaches to minimize these interferences, as well as other special precautions associated with the analysis of methylene chloride.

1.3.4 Other Potential Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination. In addition, dissolved sulfur dioxide (sulfurous acid) potentially interferes with the analysis for vinyl chloride by this method.

1.4 Alternative Sample Introduction Methods

Various alternatives are provided in SW-846 Method 8021B, Section 7.0 for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC system. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques may be found in SW-846 Methods 3500 and 5000, respectively.

Some of these alternative sample introduction methods include:

- Direct injection (SW-846 Methods 5000 and 8260B, Section 7.1.1)
- Purge-and-trap for aqueous samples (SW-846 Method 5030)
- Purge-and-trap for solid samples (SW-846 Method 5035A)
- Vacuum distillation (SW-846 Method 5032)
- Azeotropic distillation (SW-846 Method 5031)
- Automated static headspace (SW-846 Method 5021), and
- Cartridge desorption (SW-846 Method 5041)

This guidance document is primarily intended to provide QA/QC requirements and performance standards for SW-846 Method 8021B using purge-and-trap sample introduction via SW-846 Methods 5030 and 5035 for aqueous and solid samples, respectively. If other sample introduction methods are required and utilized because of analytical circumstances, the laboratory must provide a full explanation and justification in the Environmental Laboratory case narrative.

1.5 Quality Control Requirements for SW-846 Method 8021B

1.5.1 General Quality Control Requirements for Determinative Chromatographic Methods

Refer to SW-846 Method 8000 for general quality control procedures for all chromatographic methods, including SW-846 Method 8021B. These requirements include that each laboratory maintain a formal quality assurance program and records to document the quality of all chromatographic data.

Quality Control procedures necessary to evaluate the GC system operation may be found in SW-846 Method 8000, Sec. 7.0 and SW-846 Method 8021B, section 8.0, and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. Instrument quality control and method performance requirements are presented in SW-846 Method 8021B, Section 9.0.

1.5.2 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8021B

Specific QA/QC requirements and performance standards for SW-846 Method 8021B are presented in Table V D-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide an LSP with “Presumptive Certainty” regarding the usability of analytical data to support MCP decisions. The concept of “Presumptive Certainty” is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of “Presumptive Certainty” of data acceptance by agency reviewers. In order to achieve “Presumptive Certainty”, parties must:

(a) Comply with the procedures described and referenced in WSC-CAM–V D;

(b) Comply with the applicable QC requirements prescribed in Table V D-1 for this test procedure;

(c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table V D-1 for this test procedure; and

(d) Adopt the reporting formats and elements specified in the CAM

In achieving the status of "Presumptive Certainty", parties will be assured that analytical data sets:

- ✓ Will satisfy the broad QA/QC requirements of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;
- ✓ May be used in a data usability assessment, and if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered useable data to support site characterization decisions made pursuant to the MCP; and
- ✓ May be used to help support a data representativeness assessment.

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and document an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

1.5.3 Recovery of Matrix Spikes (MS) and Matrix Spike Duplicates (MSD) with Methanol-Preserved Soil/Sediment Samples

The recovery of matrix spikes from a soil/sediment sample that has been preserved with methanol cannot be used to directly evaluate matrix-related bias/accuracy in the conventional definition of these terms. Quality Control parameters expressed in terms of these percent recoveries (%R) may be more indicative of the variabilities associated with the analytical system (sample processing, introduction, and/or component separation). Because of this limitation, it is recommended that laboratory analyze standard reference materials and participate in relevant performance evaluation studies as frequently as possible. Recommended practices for additional quality assurance made be found in SW-846 Methods 5000 and 8000, respectively.

This inherent limitation of methanol preservation with respect to the evaluation of matrix spike recoveries is more than compensated for by the marked improvement in sample integrity and conservation/recoveries of the volatile analytes of concern from soil matrices by minimizing volatilization losses.

1.5.4 Recovery of Surrogates with Methanol-Preserved Soil/Sediment Samples

Analytical surrogates as described in Table V D-1 should be spiked directly into the solvent at the time of extraction. Solvent-fortified analytical surrogates provide unresolved or combined percent (%) recovery data dependent on both analytical efficiencies and sample matrix effects. To determine the source of this analytical anomaly, parties may wish and/or otherwise may need to obtain and analyze additional QC samples.

1.5.5 Trip Blanks and Field Duplicates for SW-846 Method 8021B Analyses

As described in WSC-CAM -VII A, Section 2.5, Table VII A-1, a Trip Blank for each cooler and submission of Field Duplicates are recommended for drinking water samples only. However, the Field Duplicates need only be analyzed if one or more analytes are detected in the primary sample above the Reporting Limit (RL). The cooler Trip Blank need only be analyzed if one or more analytes are detected in any sample above the Reporting Limit. Drinking water samples should be identified and specific analytical instruction for the drinking water and associated field quality control samples provided when the samples are submitted to the laboratory for analysis.

Title: **Table V D-1 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8021B**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Retention Time Windows	Laboratory Analytical Accuracy	(1) Prior to initial calibration and when a new GC column is installed. (2) Calculated according to the method. (Section 7.6 of SW-846 8000).	No	NA	NA
Initial Calibration	Laboratory Analytical Accuracy	(1) Minimum of 5 standards. (2) Low standard must be ≤ reporting limit. (3) %RSD should be ≤20 or "r" should be ≥0.99. (4) If regression analysis is used, the curve must not be forced through the origin. (5) Curves must be verified by an independent ICV before analysis.	No	Recalibrate as required by method.	Report exceedances in case narrative.
Continuing Calibration (CCAL)	Laboratory Analytical Accuracy	(1) Prior to samples, every 12 hours or every 10 samples, whichever is more frequent, and at the end of the analytical sequence. (2) Concentration level near midpoint of curve. (3) Percent difference or percent drift of calibration factors should be ≤15% with the exception of gases which should be ≤20%. (4) Verify all analytes fall within retention time windows.	No	(1) Perform instrument maintenance, reanalyze CCAL and/or recalibrate as required by method. (2) Reanalyze "batch samples" if beginning or closing CCAL exhibited low response and associated VOCs were or were not detected in samples. (3) Reanalyze "batch samples" if beginning or closing CCAL exhibited high response and associated VOCs were detected in the samples.	Report exceedances in case narrative.
Method Blanks	Laboratory Method Sensitivity (contamination evaluation)	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Matrix-specific (e.g., water, soil). (3) Target analytes must be less than or equal to reporting limit.	Yes	Locate source of contamination; correct problem; reanalyze associated samples if contaminants are present in the method blank.	(1) Report nonconformances in case narrative. (2) If contamination of method blanks is suspected or present, the laboratory, using a "B" flag or some other convention (such as the case narrative), should qualify the sample results. (3) If reanalysis is performed within holding time, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time, the laboratory must report results of both the initial analysis and reanalysis.

Title: **Table V D-1 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8021B**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Spikes (LCSs)	Laboratory Method Accuracy	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using standard source different than used for initial calibration. (3) Concentration level should be ≤ mid-level standard. (4) Must contain all target analytes. (5) Matrix-specific (e.g., soil, water). (6) Percent recoveries must be between 70-130. (7) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes	Recalculate the percent recoveries. Check MS/MSD; if recoveries are acceptable in MS/MSD, nonconformance may be isolated to LCS. If recoveries are outside criteria in MS/MSD, reanalyze associated samples.	(1) Report exceedances in case narrative. (2) If reanalysis is performed within holding time, the laboratory may report results of the reanalysis only. (3) If reanalysis is performed outside of holding time, the laboratory must report results of both the initial analysis and reanalysis.
LCS Duplicate	Laboratory Method Precision	(1) Analyzed with every batch or every 20 samples, whichever is more frequent. (2) Prepared using same standard source and concentration as LCS. (3) Must contain all target analytes. (4) Analyze immediately after LCS. (5) Laboratory–determined percent recoveries must be between 70 – 130 for target compounds (6) Matrix and preservative-specific (e.g., water, MeOH, $NaHSO_4$). (7) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 25 except for "difficult" (**) analytes which must be ≤ 50..	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances
MS/MSDs	Method Accuracy in Sample Matrix Method Precision in Sample Matrix	(1) Analyzed with every 20 samples (BATCH QC). (2) Matrix-specific. (3) Prepared using standard source different than that used for initial calibration. (4) Concentration level should be between low and mid-level standard. (5) Must contain all target analytes. (6) Percent recoveries should be between 70-130. (7) RPDs should be ≤30.	Yes (Only when requested by the data-user)	Check LCS; if recoveries acceptable in LCS, narrate nonconformance.	Report exceedances in case narrative.

Title: **Table V D-1 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8021B**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Surrogates	Accuracy in Sample Matrix	(1) Minimum of 2, one surrogate representing each detector and both surrogates must encompass range of temperature program used. Recommended surrogates: 1,4-Dichlorobutane and Bromochlorobenzene (2) Percent recoveries must be between 70-130. (3) Laboratories are expected to develop their own in-house control limits, which should fall within the limits listed above.	Yes (report surrogate recoveries from both detectors, where applicable, and from both columns when dual column confirmation is used)	If the surrogate is outside limits, reanalyze the sample on the affected detector unless obvious interference present.	(1) Report exceedances in case narrative. (2) If reanalysis yields similar surrogate nonconformances, the laboratory should report results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable surrogate recoveries, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable surrogate recoveries, the laboratory must report results of both the initial analysis and reanalysis. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.
Internal Standards *(Optional)*	Laboratory Analytical Accuracy and Method Accuracy in Sample Matrix	1) Minimum of 2, one internal standard representing each detector. Recommended internal standards: Fluorobenzene and 2-Bromo-1-chloropropane (2) Area counts in samples must be between 50 – 200% of the area counts in the associated continuing calibration standard. (3) Retention times of internal standards must be within calculated retention time windows.	No	If internal standard is outside limits, reanalyze the sample on the affected detector unless obvious interference present.	(1) Report exceedances in case narrative. (2) If reanalysis yields similar internal standard nonconformance, the laboratory should report both results of both analyses. (3) If reanalysis is performed within holding time and yields acceptable internal standard recovery, the laboratory may report results of the reanalysis only. (4) If reanalysis is performed outside of holding time and yields acceptable internal standard recovery, the laboratory must report results of both analyses. (5) If sample is not reanalyzed due to obvious interference, the laboratory must provide the chromatogram in the data report.

Title: **Table V D-1 Specific QA/QC Requirements and Performance Standards for SW-846 Method 8021B**

Required QA/QC Parameter	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Identification and Quantitation	Inter-laboratory consistency	(1) Laboratory should use the average calibration factor of each analyte for quantitation. (2) Secondary column confirmation analysis (if used): The laboratory must report the higher of the two results unless obvious interference is present on one of the columns in which case the laboratory can report the lower result. All required QA/QC parameters (e.g., calibrations, LCSs, etc.) must be met on the secondary column as well. (3) GC/MS confirmation analysis (if used): Used for qualitative confirmation of single column analyses only.	No	NA	If the RPD between the dual column results exceeds 40, the laboratory should qualify the sample results and/or note the exceedance in the case narrative. NOTE: If the high RPD can be definitively attributed to interference on one of the two columns, the laboratory should report the lower value and provide a discussion in the case narrative that this approach was employed.
General Reporting Issues	NA	(1) The laboratory must report values ≥ the sample-specific reporting limit; optionally, values below the sample-specific reporting limit can be reported as estimated, if requested. The laboratory must report results for samples and blanks in a consistent manner. (2) Dilutions: If diluted and undiluted analyses are performed, the laboratory should report results for the lowest dilution within the valid calibration range for each analyte. The associated QC (e.g., method blanks, surrogates, etc.) for each analysis must be reported.	Yes	NA	(1) Qualification of the data is required if reporting values below the sample-specific reporting limit. (2) Recommendation is that the reporting of diluted and undiluted analyses should be a must to be consistent with the inorganic reporting convention of reporting all dilutions and to ensure the lowest possible reporting limit can be achieved if the data is available.

GC = Gas Chromatography
MS/MSDs = Matrix Spikes/Matrix Spike Duplicates
%RSD = Percent Relative Standard Deviation
ICV = Initial Calibration Verification – separate source standard
"r" = Correlation Coefficient
RPDs = Relative Percent Differences

1.6 Analyte List for SW-846 Method 8021B

The MCP analyte list for SW-846 Method 8021B presented in Table VD-2 is intended to be protective of human health and the environment. The list is comprised of potential contaminants that are readily analyzable by SW-846 Method 8021B using conventional purge-and-trap sample introduction (SW-846 Method 5030 (ambient temperature)) for aqueous and closed-system purge-and-trap (SW-846 Method 5035A) for solid samples. Most of the compounded listed have a promulgated compound-specific or hydrocarbon range (e.g., C_9 – C_{10} aromatic hydrocarbons) MCP Method 1 Groundwater/Soil Standard as described in 310 CMR 40.0974 and 40.0975, respectively. The remaining volatile compounds that comprise the SW-846 Method 8021B Analyte List are designated "consensus contaminants". These volatile compounds do not have a promulgated MCP Method 1 Standards but do have MCP Reportable Concentrations (RCs) as described in 310 CMR 40.0360 and 40.1600 and published EPA Integrated Risk Information System (IRIS) toxicity values. Using available toxicity data for these "consensus contaminants", the Department has derived compound-specific MCP Method 2 Groundwater/Soil Standards as described in 310 CMR 40.0983 and 40.0984, respectively. An updated list of the Department-derived MCP Method 2 Standards may be found at the following URL:

http://www.mass.gov/dep/bwsc/files/standard/method2/method2.htm

The MCP Method 1 Groundwater/Soil Standards used to characterize the risk of harm posed by oil or hazardous materials at a disposal site are described in 310 CMR 40.0974(2), Table 1. This list of groundwater/soil standards, developed by the Department, takes into account a defined set of conservative potential exposure pathways likely to be encountered at most disposal sites. Method 1 Standards have been developed by the Department for over one hundred organic and inorganic contaminants that are commonly encountered at disposal sites. The MCP Method 1 Groundwater/Soil Standards list is periodically reviewed and updated by the Department. When compounds are added to the MCP Method 1 Groundwater/Soil Standards list that are suitable for analysis by SW-846 Method 8021B, the analyte list for this method will be updated accordingly.

MCP Method 2 Groundwater/Soil Standards are developed by the Department (or others) for contaminants of concern for which MCP Method 1 Standards have not been promulgated. The use of Department-developed MCP Method 2 Standards is discretionary. Alternatively, site-specific MCP Method 2 Standards may be developed or a Method 3 risk characterization, as described in 310 CMR 40.0990, may be conducted to evaluate or characterize the risk of harm posed by oil or hazardous materials at a disposal site.

1.6.1 Additional Reporting Requirements for SW-846 Method 8021B when a Photoionization Detector (PID) and Hall Electrolytic Conductivity Detector (HECD) are used in Series

While it is not necessary to request and report all the SW-846 Method 8021B analytes listed in Table V B-2 to obtain Presumptive Certainty, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Uncharacterized sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or
- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

Note that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is <u>not</u> a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain Presumptive Certainty status.

The Reporting Limit (based on the concentration of the lowest calibration standard) for each contaminant of concern must be less than or equal to the MCP standards or criteria that the contaminant concentrations are being compared to (e.g., Method 1 Standards, RfDs, benchmark values, background, etc.) <u>with the exceptions footnoted in Table V D-2</u>. Meeting "MCP program" reporting limits may require analytical modifications, such as increased sampling weight or volume or to increase sensitivity. All such modifications must be described in the Environmental Laboratory case narrative.

1.6.2 Additional Reporting Requirements for SW-846 Method 8021B when a Photoionization Detector (PID) and Hall Electrolytic Conductivity Detector (HECD) are used Independently

For disposal sites that have been adequately characterized in previous sampling rounds a volatile aromatic or chlorinated subset of the total analyte list of SW-846 Method 8021B may be requested at the discretion of the LSP from the laboratory. The volatile aromatic compound sub-list is comprised of all compounds with the designation "PID" on Table V D-2 under Primary detector. The volatile chlorinated compound sub-list is comprised of all compounds with the designation "HECD" on Table V D-2 under Primary Detector.

Analytes	CASRN [a]	Primary Detector(s)	MCP CLEANUP STANDARDS	
			GW-1	S-1/GW-1
			µg/L (ppb)	µg/g (ppm)
Benzene	71432	PID	5	10
Bromodichloromethane	75274	HECD	5	0.1
Bromoform	75252	HECD	5	0.1
Carbon Tetrachloride	56235	HECD	5	1
Chlorobenzene	108907	HECD	100	8
Chloroethane [SX]	75003	HECD	X[1]	X[1]
Chloroform	67663	HECD	5	0.1
Chloromethane [SX]	74873	HECD	X[1]	X[1]
Chlorotoluene, 2-	95498	HECD	X[1]	X[1]
Chlorotoluene, 4-	106434	HECD	X[1]	X[1]
Dibromochloromethane	124481	HECD	5	0.09
Dichlorobenzene, 1,2- (o-DCB)	95501	HECD	600	100
Dichlorobenzene, 1,3- (m-DCB)	541731	HECD	600	100
Dichlorobenzene, 1,4- (p-DCB)	106467	HECD	5	2
Dichlorodifluoromethane (Freon 12) [SX]	75718	HECD	X[1]	X[1]
Dichloroethane, 1,1-	75343	HECD	70	3
Dichloroethane, 1,2-	107062	HECD	5	0.05[2]
Dichloroethylene, 1,1-	75354	HECD	7	0.7
Dichloroethylene, *cis*-1,2-	156592	HECD	70	2
Dichloroethylene, *trans*-1,2-	156605	HECD	100	4
Dichloropropane, 1,2-	78875	HECD	5	0. 1
Dichloropropane, 1,3-	142289	HECD	X[1]	X[1]
Dichloropropene, -1,3- [SX,3]	10061015	HECD	0.5	0.01[2]
Ethylbenzene	100414	PID	700	80
Ethylene Dibromide (EDB)	106934	HECD	0.02[2]	0.005[2]

Analytes	CASRN [a]	Primary Detector(s)	MCP CLEANUP STANDARDS	
			GW-1	S-1/GW-1
			µg/L (ppb)	µg/g (ppm)
Table V D-2 (Page 2 of 2)				
Hexachlorobutadiene	87683	HECD	0.6[2]	3
Methylene Chloride	75092	HECD	5	0.1
Naphthalene	91203	PID	20	4
Styrene [SX]	100425	PID	100	2
Tetrachloroethane, 1,1,1,2-	630206	HECD	5	0.4
Tetrachloroethane, 1,1,2,2-	79345	HECD	2	0.02[2]
Tetrachloroethylene	127184	HECD	5	0.5
Toluene	108883	PID	1000	90
Trichlorobenzene, 1,2,4-	120821	HECD	70	100
Trichloroethane, 1,1,1-	71556	HECD	200	30
Trichloroethane, 1,1,2-	79005	HECD	5	0.3
Trichloroethylene	79016	HECD	5	0.4
Vinyl Chloride [SX]	75014	HECD	2	0.3
Xylene, m-[4]	108383	PID	10,000[1]	500[1]
Xylene, o-[4]	95476	PID	10,000[1]	500[1]
Xylene, p-[4]	106423	PID	10,000[1]	500[1]

CASRN - Chemical Abstract Service Registry Number

PID – Photoionization Detector

HECD - Hall Electrolytic Conductivity Detector

SX -compounds are potentially unstable and susceptible to acid hydrolysis, abiotic degradation and/or loss during storage

1 Department-Developed MCP Method 2 Standard. Use of these Standards is discretionary. See URL: http://www.mass.gov/dep/bwsc/files/standard/method2/method2.htm

2. Standard RL for this compound may not be able to achieve regulatory compliance limit
3. Regulated as 1,3-Dichloropropene, Mixed Isomers (CASN:542756) . Report as the additive sum of the concentrations of *cis*-1,3-Dichloropropene and *trans*-1,3-Dichloropropene
4. Regulated as Xylenes (Mixed Isomers). Report as Total Xylenes or as individual Xylene isomers, if recoverable chromatographically.

2.0 Data Usability Assessment for SW-846 Method 8021B

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 8021B which may be used to directly assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

3.0 Reporting Requirements for SW-846 Method 8021B

3.1 General Reporting Requirements for SW-846 Method 8021B

General environmental laboratory reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM VII A, Section 2.4. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including:

- Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
- Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
- Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
- Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
- Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
- Environmental Laboratory Case Narrative contents in WSC-CAM-VII A, Section 2.4.5, and
- Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 8021B

Specific Quality Control Requirements and Performance Standards for SW-846 Method 8021B are presented in Table V D-1. Specific reporting requirements for SW-846 Method 8021B are summarized below in Table V D-3 as “Required Analytical Deliverables (**YES**)”. These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as “Required Analytical Deliverables (**NO**)”, these data are to be available for review during an audit and may also be requested on a client-specific basis.

3.2.1 Data Correction for VOC Concentration Calculations for Methanol Preservation Dilution Effect

Based on the requirements of SW-846 Method 8000C, Section 11.10.05, VOC analytical results for soil/sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting volatile organic concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases, if this correction is neglected.

VOC concentrations and the recovery of matrix spikes and/or surrogates in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the assumption that 1 g of water occupies a volume of 1 mL). This is a conservative correction regarding calculated VOC concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical binding forces. The total solvent/water volume (Vt) is calculated using the following equation:

$$\text{nL solvent/water (Vt)} = \text{nL of methanol} + ((\%\ \text{moisture}/100) \times \text{g of sample})$$

This "corrected" Vt value should be substituted directly for the Vt value in the equation shown in SW-846 Method 8000. Section 7.10.1.2. It should be noted that whether corrected or uncorrected, the Vt value used to calculate VOC concentrations must also take into consideration the volume of any surrogate/spiking solution added to soil/sediment samples

3.2.2 Sample Dilution

Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard or any non-target peak exceeds the dynamic range of the detector (i.e., "off scale"), the Reporting Limit (RL) for each VOA target analyte must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Aliquot Volume (mL)} + \text{Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

RL_d = DF X Lowest Calibration Standard for Target Analyte

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the Environmental Laboratory case narrative.

Table V D-3 Routine Reporting Requirements for SW-846 Method 8021B

Parameter	Required Analytical Deliverable
Retention time Windows	***NO***
Initial Calibration	***NO***
Continuing Calibration (CCAL)	***NO***
Method (Preparation) Blank	***YES***
Laboratory Control Spikes (LCSs)	***YES***
LCS Duplicates (LCSDs)	***YES***
Matrix Spike Sample (MS)	***YES (if requested field MS)***
Matrix Spike Duplicate (MSD)	***YES (if requested field MS/MSD)***
Field Matrix Duplicate (MD)	***YES (if requested field MD***
Surrogates	***YES***
Internal Standards (ISs)	***NO***
Identification and Quantification	***NO***
General Reporting Issues	***YES***

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for volatile organic compounds analyzed in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-WSC-CAM–VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data Conducted in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)". The selection of preservation for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

Aqueous Samples

Matrix	Analyte	Container [1]	Preservative [2]	Holding Time
Aqueous Samples, with no Residual Chlorine	Most Volatile Organic Compounds	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	Adjust pH to < 2.0 by addition of HCl or $NaHSO_4$. to container before sampling. **Cool 4 ± 2° C.**	14 days
	MTBE or other fuel oxygenates *only* **with heated purge-and-trap sample introduction**	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	0.7 g of trisodium phosphate dodecahydrate (TSP) per 40 ml. **Verify pH > 11.0. Cool 4 ± 2° C.**[3]	14 days
	Reactive[4] volatile organics susceptible to acid hydrolysis, abiotic degradation or loss during storage	(2) x 40-mL VOC vials w/ Teflon-lined septa screw caps and protect from light.	**Cool 4± 2° C.**	Analyze ASAP but not more 7 days [5,6]
Aqueous, with Residual Chlorine	Presence of chlorine residual is usually associated with drinking water samples. Collect sample in at least two (2) x 40-mL VOC vials w/ Teflon-lined septa screw caps ***containing*** either 25 mg of Ascorbic A cid or 3 mg of Sodium Thiosulfate. **If Residual Chlorine > 5 mg/L additional dechlorination agent may be required** After dechlorination is confirmed, preserve as above based on compound classes			

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis.

2 Preservation of samples by acidification to pH < 2.0 and analysis within 14 days is considered a suitable preservation technique for samples not expected to contain reactive contaminants of concern.

3 TSP may also be used to preserve samples for BTEX and/or VPH analysis (i.e., it would not be necessary to obtain samples in separate vials).

4 While there are chemicals that are described as *potentially* reactive on the list of Target Analytes (see Table II A-2), at this time DEP does not consider any chemicals on this list to be "reactive" and requiring special preservation and/or hold times.

5. Every reasonable effort should be made to analyze reactive samples as soon as possible (the goal should be 24 hours or sooner) after the time of collection. In all cases the holding time for reactive samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

6. In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (e.g., acid preservation/with cooling for BTEX and no acid preservation/cooling-only for reactive compounds) separate sampling containers to accommodate the different preservation techniques may be required. The selection of preservation technique for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

Soil, Sediment and Waste Samples

Matrix	Container [a]	Preservation[1,2]	Holding Time[3]
Soil/Sediment Samples ***High-Level Analysis***	Extrude 5 grams of sample directly into a pre-weighed vial* w/ Teflon-lined septa screw caps: Vials must contain 1 mL purge-and-trap grade methanol for every g soil/sediment. *(1) x 60-mL vial or (1) x 40-mL vial	Cool to 4 ± 2° C; protect from light	14 days Up to 1 year for samples frozen within 24 hours of collection
	5 g EnCore samplers[4] or other suitable coring device	Cool to 4 ± 2° C in field and deliver to laboratory within 48 hours of collection for freezing (< -7° C) or methanol preservation.	
Soil/Sediment Samples ***Low-Level Analysis*** by Closed-System Purge-and-Trap Process (SW-846 Method 3035A)	5 g EnCore samplers[4] or other suitable coring device.	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection (see Note 1). Alternatively, samples may be frozen to < -7° C in the field using gel packs	14 days Up to 1 year for samples frozen within 24 hours of collection
	Extrude 5 grams of sample directly into (2) x pre-weighed 40 ml VOC vials containing 5 mL of reagent water (with or without chemical preservation; see Note 1) and a Teflon-coated magnetic stir bar[5].	Cool to 4 ± 2° C in field and deliver to laboratory for freezing (< -7° C) or analysis within 48 hours of sample collection. Alternatively, samples may be frozen to < -7° C in the field using gel packs	
Waste Samples	Collect sample in one (1) x 500 mL amber wide mouth jar with a teflon lined screw cap.	No special preservation required	14 days

a. The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised during shipping and/or analysis. Caution: samples to be frozen should not be stored vertically. These samples must be stored horizontally or at least at a 45 degree angle to avoid breakage from expansion.

1. For biologically active soils, immediate chemical or freezing preservation is necessary due to the rapid loss of BTEX compounds within the first 48 hours after sample collection.

2 A number of acceptable alternative preservation techniques requiring close communication with the receiving laboratory that require field cooling (4 ± 2°) with subsequent laboratory preservation (freezing, methanol, $NaHSO_4$, etc.) and/or expedited analysis (48 hours) are presented in Appendix A, "Collection and Preservation* of Aqueous and Solid Samples for Volatile Organic Compounds (VOC) Analyses" of the document entitled , "Closed System Purge-and-Trap and Extraction for Volatile Organics In Soil and Waste Systems", an updated version of SW-846 Method 5035A published by US EPA In July 2002. http://www.epa.gov/epaoswer/hazwaste/test/pdfs/5035a_r1.pdf

3 Holding time is calculated from the time of sample collection and only applies to samples that have been frozen and chemically preserved.

4. EnCore Sampler may not be suitable for certain soil types; refer to guidance in SW-846 Method 5035A

5. Not required if Closed-System Purge-and Trap device employs a means of stirring the sample other than a magnetic stirrer

Additional Sample Handling and Preservation Notes:

Aqueous Samples:

. The most common preservation technique for aqueous samples analyzed for volatile organic compounds is the addition of HCl to the container before sampling (pH to < 2.0) and cooling to 4 + 2^{O} C. As indicated in the table above, some classes of analytes (reactive, MTBE and other fuel oxygenates if heated purge and trap is used for analysis, etc.) may require alternative preservation techniques because of their reactivity or volatility. In the unusual circumstance that contaminants of concern at a disposal site require mutually exclusive preservation techniques (acid preservation/with cooling for BTEX and no acid preservation/with cooling for reactive compounds) separate sampling containers to accommodate the different preservation techniques may be required. In all cases the selection of preservation technique for samples analyzed for volatile organic compounds should be based on the data quality objectives of the sampling program.

. If effervescence occurs upon addition of HCl, samples should be collected without the acid preservative. In these instances, the analysis holding time is seven (7) days from date collected to date analyzed.

Low-Level and High-Level Solid Samples:

An extra aliquot of sample must be collected in a 4 oz. glass jar with no preservative so that the laboratory can perform a percent solids analysis. If the same sample is being submitted to the laboratory for additional analyses which require no preservative, the percent solids analysis can be measured using an aliquot from these bottles. Otherwise, a separate bottle will be needed.

Sample Preparation Prior to Analysis

The sample must be allowed to warm to room temperature. Surrogates, internal standards, and 5 mLs of water are added to the sample vial through the septum seal, and the sample is analyzed on the closed system purge and trap.

The appropriate surrogates must be immediately added to the sample through the septum seal. The sample must be allowed to warm to room temperature. All samples must be shaken for 2 minutes prior to analysis. A 100 microliter (uL) aliquot of the methanol extract must then be removed and injected into 5 mL of purge water and the internal standards added to the 5 mL of purge water.